TRENDS AND DYNAMICS OF CHLORDANES IN THE COASTAL ATMOSPHERE OF THE MID-ATLANTIC UNITED STATES

The atmospheric transport and deposition of organochlorine pesticides is known to be a significant source of these chemicals to northern latitudes and the arctic [1-3]. Atmospheric transport of these chemicals into midlatidude ecosystems such as the Great Lakes and Chesapeake Bay is also significant[4-6]. To assess the transport and dynamics of chlordanes and other persistent organic pollutants (POPs) in the coastal, urban, suburban and rural mid-Atlantic region, we have initiated an air research and monitoring network in New Jersey (USA). This network of air and rain samplers will offer better understanding of local, regional and long range atmospheric transport and impacts to this highly industrial and populous region. Here we present data from 20 months of operation as well as a summer intensive intended to elucidate diurnal variability. Back trajectory analyses have been used to explain concentrations that deviate substantially from expected values.

Material and Methods

The atmospheric measurements and sample collections were made at three sites in New Jersey: New Brunswick (suburban), Sandy Hook (coastal marine), and Liberty State Park (urban/industrial). At each site, 24-hour integrated air samples were collected every 6 days using quartz fiber filters followed by PUF adsorbent. After one year the sampling frequency was changed to once in 9 days to match other long term monitoring programs. Integrated, wet-only precipitation samples were collected every 12 (or 18) days using MIC collectors with 0.21 m^2 stainless steel surfaces and attached glass columns filled with XAD2 resin. Additionally, an intensive sampling period was undertaken in the summer of 1998, which included air and water sampling from the Raritan Bay and lower Hudson River estuary. These samples were 12 hour samples that reflect diurnal signals and day only (ship). Samples were extracted with petroleum ether (PUF), dichloromethane (filter) and acetone/hexane (XAD), cleaned up and separated on columns packed with alumina. Samples were analyzed for chlordane (cis/trans), MC5, nonachlor (cis/trans) and oxychlordane using a HP 6890 GC/5973 MS in EI mode and selective ion monitoring. Correlative measurements of TSP, PM2.5 and particulate OC and EC with supporting meteorological measurements (wind speed and direction, rainfall intensity, temperature) were also made. Back trajectory estimates were obtained by using the NOAA Hysplit models.

Results and Discussion

Continuous measurement of chlordanes as well as other POPs in New Jersey has yielded results not unlike other research. ∑ Chlordane concentrations (sum chlordanes = trans/cis chlordane and trans/cis nonachlor) fit well within a latitudinal gradient observed by other researchers (Table 1). Average ∑chlordane concentrations were similar for both suburban and coastal sites, 135 and 118 pg/m^3 respectively. Trans/cis chlordane ratios also fit well within the north to south gradient for both sites (1.1 and 1.2 for New Brunswick and Sandy Hook respectively). The ratio is diagnostic of the "relative" weathering of the trans isomer, which is oxidized to oxychlordane.

Annual variation in ∑chlordane concentration vary with inverse temperature (1/T, Figure 1) as seen in other work[7,8]. High concentrations occurred in July and lowest concentrations were in December. When a concentration vs. 1/temperature regression was plotted, ~25% of the residuals were greater than one standard deviation (Figure 2). Those residuals greater than one standard deviation were checked against three day back trajectories at the beginning, middle and end of the sampling period[9].

Most days with concentrations greater than one standard deviation from the regression line were shown to come from either the southern part of the United States or from central Canada and/or Great Lakes regions (Figure 3). Only one day with a high residual occurred when temperatures were close to 0^{o}C. Almost all of the high residuals, both positive and negative, occur when air temperatures exceed 17^{o}C.

The trans chlordane isomer can be oxidized to oxychlordane by both biotic[10] and possibly by abiotic processes. During summer intensive sampling (12 hour day and night sampling), there is evidence of diurnal variation of trans chlordane oxidation. This oxidation is evident in both the ratio of tran/cis chlordane and trans chlordane/oxychlordane. Trans/cis chlordane ratios are 1.05 during the day and 1.2 at night. Trans chlordane/oxychlordane ratios are higher at night by a factor of two, indicating more oxychlordane is present during daytime hours. This diurnal change in both trans chlordane and oxychlordane suggests a photochemical oxidation process that needs further clarification. Daily variation of ∑Chlordane is too dependent upon other factors to show any diurnal variability, and the mean is the same for day and night samples at both New Brunswick (suburban) and Sandy Hook (coastal).

References

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Table 1.	∑ Chlordane (pg/m^3)	Trans/Cis
Arctic	**4.0 ± 0.1**	**0.8 ± 0.1**
(Patton et al, 1991; Hoff and Chan, 1986)		
Eagle Harbor	**13 ± 12**	**1.0 ± 0.2**
Sleeping Bear Dunes	**22 ± 20**	**1.0 ± 0.2**
Sturgeon Point	**37 ± 29**	**0.9 ± 0.3**
(Cortes and Hites)		
Egbert, ONT	**39 ± 35**	**1.0 ± 0.3**
(Hoff et al, 1992)		
New Brunswick, NJ	**135 ± 113**	**1.1 ± 0.1**
Sandy Hook, NJ	**118 ± 117**	**1.2 ± 0.1**
(this study)		
Columbia, SC	**300 ± 147**	**1.6 ± 0.4**
(Bidleman et. al., 1998)		
College Station, TX	**1050 ± 180**	
(Atlas and Giam, 1988)		
Midwest Soils		**1.1 ± 0.5**
(Aigner et. al, 1998)		
Technical Chlordane		**1.85**
Technical Chlordane at equilibrium with air at 20°C		**1.30**
(Bidleman et. al., 1998)		

Figure 1. Average monthly concentration for ∑ chlordane in New Jersey air 1997-1998.

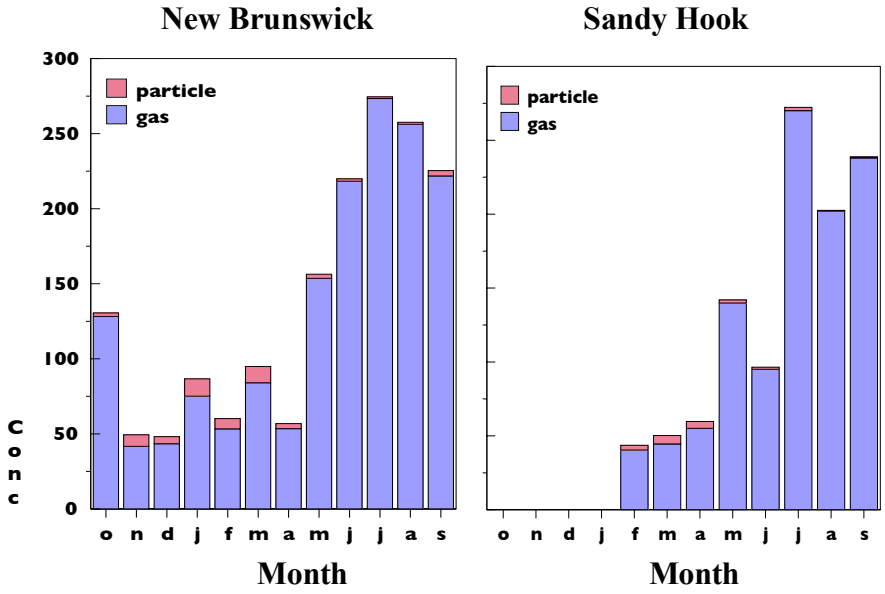

Figure 2. Trans chlordane concentration vs. 1000/T . Triangles represent concentrations greater than one standard deviation from regression; squares represent concentrations less than one standard deviation from regression.

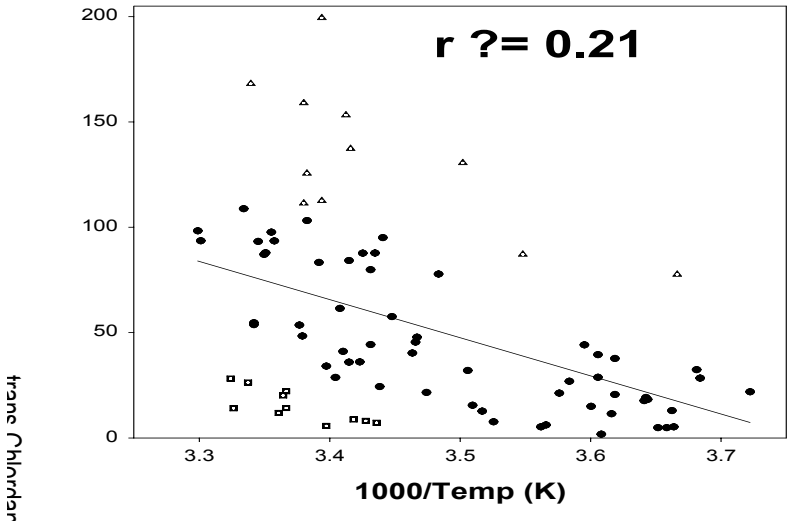

Figure 3. Three day back trajectories for outlying samples.

March 12, 1998 $\sum$ *chlordanes =4.9 pg/m*^{3} *September 9, 1997* $\sum$ *chlordanes =287 pg/m*^{3}